

UNIT FOUR

ENTROPY

Reversible part of the second law

So far we were dealing with PV diagrams, which is useful only for handling hydrostatic systems. In order to account all systems we generalise the PV diagram as work diagram. Any product of two variables giving work will do for this. These two variables are called generalised force and generalised displacement. Some combinations are given below.

System	Generalised force	Generalised displacement	Work done
Hydrostatic system	Pressure P	Volume V	PdV
Wire	Tension T	Length L	TdL
Surface film	Surfacetension S	Area A	SdA
Electrochemical cell	emf, ϵ	Charge q	ϵdq
Dielectric substance	Electric field E	Dipolement p	Edp

In work diagrams, generalised force is taken along the vertical axis (Y) and the generalised displacement is taken along the horizontal axis. In a work diagram the isothermal processes and adiabatic processes can be indicated by different curves for all systems.

Here we discuss how the reversible part of second law of thermodynamic leads to Clausius' theorem.

Consider a reversible process represented by the curve AB as shown in figure 4.1. The dashed curves through A and B represent adiabatic processes 1 and 2 respectively. Draw a line ab from the adiabatic curve 1

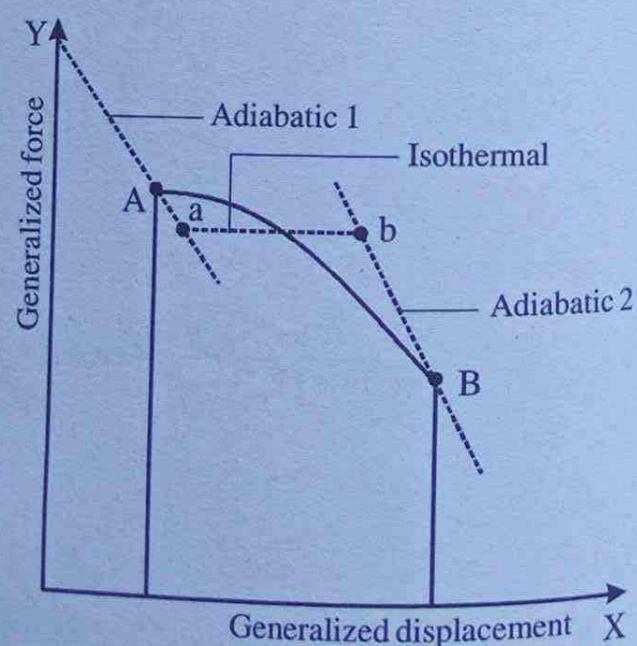


Figure 4.1

to adiabatic curve 2. The curve ab represents an isothermal process. This curve is drawn in such a way that the area under AB is equal to area under AabB. Then the work done in both the paths is the same.

Using first law of thermodynamics

$$Q_{AB} = U_B - U_A + W_{AB}$$

and

$$W_{AB} = W_{AabB}, \text{ we get}$$

$$Q_{AB} = Q_{AabB}$$

since no heat is transferred in transversing from A to a and b to B (adiabatic paths), we have

$$Q_{AB} = Q_{ab} \quad \dots\dots (1)$$

This discussion shows that we can go from an initial state to a final state of a system in two ways such that heat transferred is the same, one along $A \rightarrow B$ (isothermal process) the other along $A \rightarrow a \rightarrow b \rightarrow B$ (adiabatic \rightarrow isothermal \rightarrow adiabatic). This reversible process enables us to develop a new concept.

Clausius' theorem

Consider a reversible cycle ABCDA on the work diagram. The closed curve can be divided into large number of Carnot cycles by drawing adiabatics and isothermals as shown in figure below. since no two adiabatic lines can intersect, a number of lines may be drawn, dividing the circle into a number of adjacent strips. A zigzag

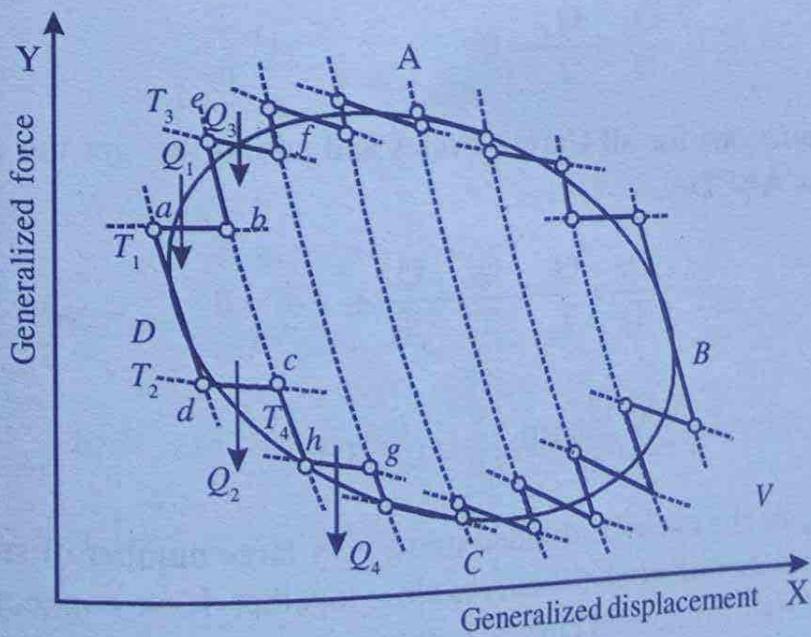


Figure 4.2

closed path may now be drawn consisting of alternate adiabatic and isothermal portions such that heat transferred during all the isothermal portions is equal to the heat transferred in the original cycle.

Consider the Carnot cycle abcda. During the isothermal process ab at temperature T_1 , heat Q_1 is absorbed, during the isothermal process cd at temperature T_2 , heat Q_2 is rejected.

From the efficiency of the Carnot cycle we have

$$\text{or } \frac{Q_1}{Q_2} = \frac{T_1}{T_2}$$

$$\therefore \frac{Q_1}{T_1} = \frac{Q_2}{T_2} \quad \dots\dots (2)$$

Applying the sign convention to Q , Q_1 is positive (absorbed) Q_2 is negative (rejected)

$$\text{i.e. } \frac{Q_1}{T_1} = -\frac{Q_2}{T_2}$$

$$\text{or } \frac{Q_1}{T_1} + \frac{Q_2}{T_2} = 0$$

Similarly the Carnot cycle efghe, we can write

$$\frac{Q_3}{T_3} + \frac{Q_4}{T_4} = 0$$

Writing equations for all Carnot cycles and adding we get the equation for the cyclic process ABCDA.

$$\text{i.e. } \frac{Q_1}{T_1} + \frac{Q_2}{T_2} + \frac{Q_3}{T_3} + \frac{Q_4}{T_4} + \dots\dots = 0$$

$$\text{or } \sum_i \frac{Q_i}{T_i} = 0, \quad i = 1, 2, 3, 4, \dots\dots \quad \dots\dots (3)$$

Now imagine the cycle be divided into a very large number of strips by drawing a very large number of adiabatic curves close together. If we connect these adiabatic curves with small isothermal curves, in the manner already described then a zigzag

path may be traced that can be made to approximate the original cycle as close as we please. When these isothermal processes become infinitesimal, $\frac{Q}{T}$ becomes $\frac{dQ}{T}$, the summation in the equation can be replaced by integral over a closed path. Thus we have

$$\oint_R \frac{dQ}{T} = 0 \quad \dots\dots (4)$$

R indicates that it is valid only for reversible cycle. This result is known as Clausius' theorem. This is one part of Clausius' mathematical statement of the second law of thermodynamics. The other part is for irreversible cycle.

Entropy

Consider a thermodynamic system taken from the initial state A to state B along the path ACB (say R_1) then from B to A along the path BDA (say R_2). The two paths together form a reversible cycle. According to Clausius' theorem

$$\oint_{R_1 R_2} \frac{dQ}{T} = 0 \quad \dots\dots (5)$$

This can be written as

$$\int_{R_1 A}^B \frac{dQ}{T} + \int_{R_2 B}^A \frac{dQ}{T} = 0$$

or

$$\int_{R_1 A}^B \frac{dQ}{T} = - \int_{R_2 B}^A \frac{dQ}{T} = 0$$

Since path R_2 is reversible

$$\int_{R_1 A}^B \frac{dQ}{T} = \int_{R_2 A}^B \frac{dQ}{T} = 0 \quad \dots\dots (6)$$

The paths R_1 and R_2 are chosen arbitrarily. It shows that $\int \frac{dQ}{T}$ is independent of the reversible path connecting between A and B and depends only on the initial

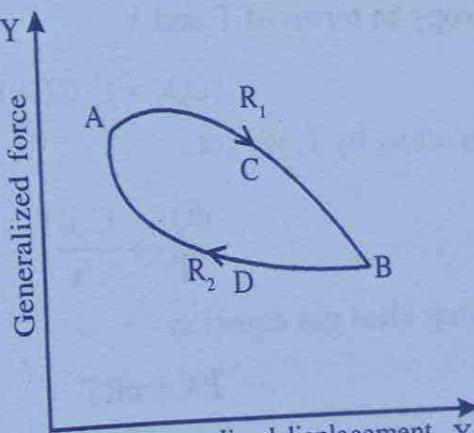


Figure 4.3

state A and the final state B. This integral indicates that there exists a function of thermodynamic coordinates of a system which depends only on the initial and final states. This is called entropy denoted by S. It may be noted that it is a state function. If S_A is the entropy at the initial state A and S_B is the entropy at the final state B given by

$$S_B - S_A = \int_{RA}^B \frac{dQ}{T} \quad \dots\dots (7)$$

It may further be noted that heat entering a system depends on path whereas entropy is not.

If the states A and B are infinitesimally close, the change in entropy is also infinitesimal and is denoted by dS . Then equation 7 becomes

$$dS = \frac{dQ_R}{T} \quad \dots\dots (8)$$

dS is an exact differential since it is the differential of an actual function, whereas dQ and dW are not. dQ_R indicates that a small quantity of heat is transferred reversibly.

The unit of entropy is JK^{-1} .

Entropy of the ideal gas

Consider an ideal gas occupying volume V at pressure P and temperature T. Let dQ_R be the infinitesimal amount of heat supplied to the gas. According to first law of thermodynamics, we have

$$dQ_R = dU + dW$$

Entropy in terms of T and V

$$dQ_R = C_V dT + PdV$$

Dividing by T, we get

$$\frac{dQ_R}{T} = \frac{C_V dT}{T} + \frac{PdV}{T}$$

Using ideal gas equation

$$PV = nRT$$

$$\frac{P}{T} = \frac{nR}{V}$$

$$\frac{dQ_R}{T} = \frac{C_V dT}{T} + \frac{nR dV}{T}$$

..... (9)

Now we calculate the entropy change when the system goes from an arbitrarily initial state T_r, V_r to other state T, V .

Integrating the above equation between these two states assuming C_V is a constant we get

$$\int \frac{dQ_R}{T} = \int_{T_r}^T C_V \frac{dT}{T} + nR \int_{V_r}^V \frac{dV}{V}$$

$$S - S_r = C_V \ln \frac{T}{T_r} + nR \ln \frac{V}{V_r}$$

$$S - S_r = C_V \ln T - C_V \ln T_r + nR \ln V - nR \ln V_r$$

$$S - S_r = C_V \ln T + nR \ln V - (C_V \ln T_r + nR \ln V_r)$$

or $S = C_V \ln T + nR \ln V - (-S_r + C_V \ln T_r + nR \ln V_r)$

$$S = C_V \ln T + nR \ln V + S_0 \quad \dots \dots (10)$$

where $S_0 = S_r - C_V \ln T_r - nR \ln V_r$

S_0 is called standard state entropy once the standard reference is chosen and the absolute entropy S can be calculated.

From equation 9, we have

$$dS = \frac{C_V dT}{T} + \frac{nR dV}{V}$$

Integrating this equation, we get

$$S = C_V \ln T + nR \ln V + S_0 \quad \dots \dots (11)$$

comparing equations 11 and 10 the standard reference turns out to be the constant of integration.

If C_V is not constant we have

$$\Delta S = \int_A^B C_V \frac{dT}{T} + nR \ln \frac{V_B}{V_A}$$

or $\Delta S = n \int_A^B c_V \frac{dT}{T} + nR \ln \frac{V_B}{V_A}$

Entropy in terms of T and P

Recall the other form of first law of thermodynamics

$$dQ_R = C_p dT - V dP$$

Dividing by T, we get

$$\frac{dQ_R}{T} = C_p \frac{dT}{T} - \frac{V dP}{T}$$

Using $PV = nRT$

$$\frac{V}{T} = \frac{nR}{P}$$

$$\therefore \frac{dQ_R}{T} = C_p \frac{dT}{T} - \frac{nR dP}{P} \quad \dots\dots (12)$$

Suppose the system goes from an initial reference state (T_r, P_r) to another state (T, P) .

Integrating the above equation by assuming C_p is a constant, we get

$$S - S_r = C_p \ln \frac{T}{T_r} - nR \ln \frac{P}{P_r}$$

or $S - S_r = C_p \ln T - nR \ln P - C_p \ln T_r + nR \ln P_r$

or $S = C_p \ln T - nR \ln P + S_r - C_p \ln T_r + nR \ln P_r$

$$S = C_p \ln T - nR \ln P + S_0 \quad \dots\dots (13)$$

where $S_0 = S_r - C_p \ln T_r + nR \ln P_r$

called standard reference entropy once S_0 is chosen, the absolute entropy S can be calculated.

If C_p is not constant, we have

$$\Delta S = \int_A^B C_p \frac{dT}{T} - nR \ln \frac{P_B}{P_A}$$

or

$$\Delta S = n \int_A^B C_p \frac{dT}{T} - nR \ln \frac{P_B}{P_A}$$

where A is the initial state and B is the final state.

Entropy in terms of P and V

We have

$$dQ_R = dU + PdV$$

$$dQ_R = C_V dT + PdV$$

or $dQ_R = C_V dT + PdV \dots\dots (14)$

Using $PV = nRT$

Take the differential on both sides

$$PdV + VdP = nRdT$$

Collect dT and put in equation 14, we get

$$dQ_R = \frac{C_V}{nR} (PdV + VdP) + PdV$$

Dividing by T

$$\frac{dQ_R}{T} = \frac{C_V P dV}{nRT} + \frac{C_V V dP}{nRT} + \frac{P dV}{T}$$

$$\text{or } \frac{dQ_R}{T} = \frac{C_V P dV}{PV} + \frac{C_V V dP}{PV} + \frac{nR dV}{V}$$

$$\frac{dQ_R}{T} = C_p \frac{dV}{V} + C_v \frac{dP}{PV} + nR \frac{dV}{V} \dots\dots (15)$$

Combining first and the last terms then use $C_p = C_v + nR$

$$\frac{dQ}{T} = C_p \frac{dV}{V} + C_v \frac{dP}{P} \dots\dots (16)$$

Integrating we get

$$\Delta S = C_p \ln V + C_v \ln P + C \dots\dots (17)$$

where C is the constant of integration. Here we assumed that C_p and C_v are constants.

TS diagram

For every infinitesimal amount of heat transfer during an infinitesimal reversible process we have

$$\frac{dQ_R}{T} = dS$$

or

$$dQ_R = TdS$$

Suppose the system goes from initial state A to final state B. Integrating between the states A and B, we get

$$Q_R = \int_A^B TdS \quad \dots\dots (18)$$

The integral on the L.H.S can be interpreted as the area under the curve ($\int ydx$) in which T is plotted on the Y-axis and S along the X-axis. Such a diagram is called TS diagram.

This idea enriches our knowledge of understanding the thermodynamic system. To describe a thermodynamic system we require two independent variables. Among several possibilities like (P, V), (P, T), (V, T), we take the pairs (T, S). The value of T and S can completely specify the thermodynamic state of the system.

The thermodynamic changes in the state of a system can be graphically represented by plotting entropy (S) along the horizontal axis and temperature T along the vertical axis. Such a diagram is called Temperature-entropy (TS diagram) diagram. TS diagrams are convenient and useful in the case of reversible cycles. This is because an isothermal process will, on such a diagram, be represented by a horizontal line drawn parallel to the entropy axis. Similarly an adiabatic process will be represented by a vertical line parallel to the temperature axis. This is because, we have

$dQ_R = \frac{dS}{T}$, for an adiabatic process $dQ = 0$ implies $dS = 0$. So S is a constant such a process is called isentropic process. For a reversible isobaric process the curve has a slope that can be obtained from

$$dS = C_p \frac{dT}{T} - nR \frac{dP}{P} \text{ see eq 12}$$

For an isobaric process, $dP = 0$

$$dS = C_p \frac{dT}{T}$$

$$\left(\frac{\partial T}{\partial S} \right)_p = \frac{T}{C_p} \quad \dots \dots (19)$$

or

$\left(\frac{\partial T}{\partial S} \right)_p$ is the slope of the TS diagram at constant pressure.

Similarly for a reversible isochoric process, the graph is curve which has a slope that can be obtained from

$$dS = \frac{C_v}{T} dT + nR \frac{dV}{V} \quad (\text{see eq 9})$$

For an isochoric process $dV = 0$

$$dS = \frac{C_v}{T} dT$$

$$\text{or} \quad \left(\frac{\partial T}{\partial S} \right)_v = \frac{T}{C_v} \quad \dots \dots (20)$$

$\left(\frac{\partial T}{\partial S} \right)_v$ is the slope of the TS diagram at constant pressure. The isochoric, isobaric, isentropic and isothermal curves are shown in figure below.

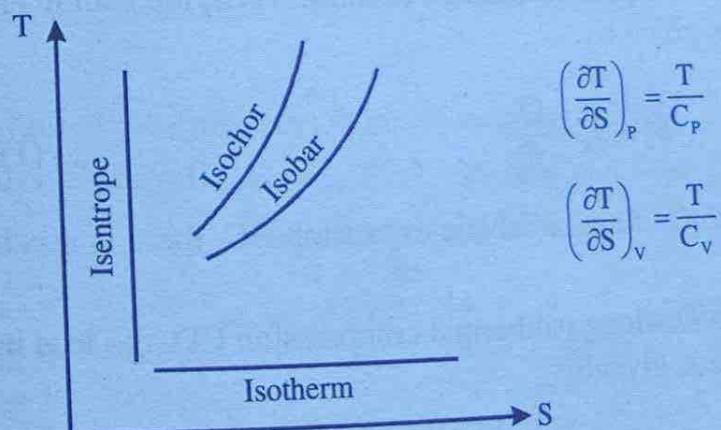
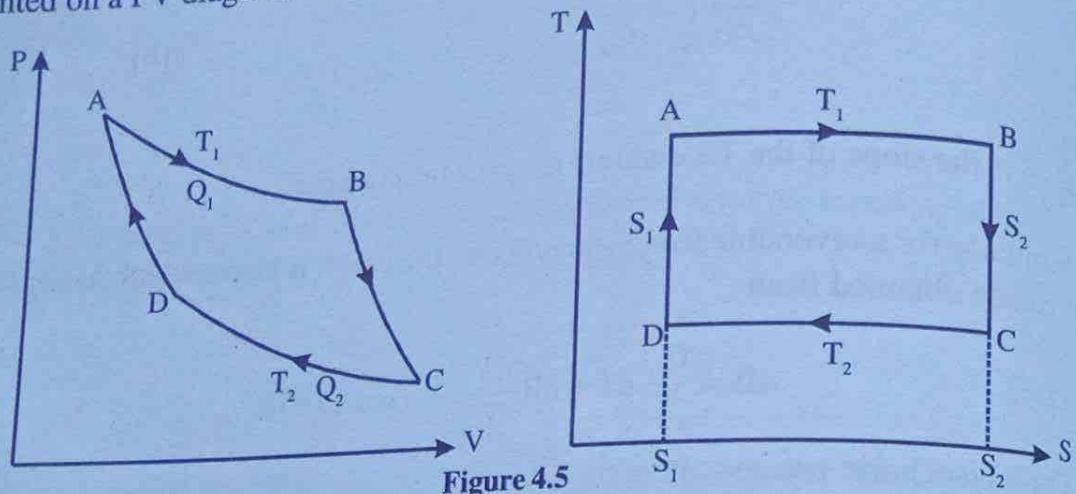


Figure 4.4

TS diagram for a Carnot cycle

A Carnot cycle consists of two isotherms and two adiabatics. When it is represented on a PV diagram we get a figure as shown below.



AB and CD are isotherms at temperatures T_1 and T_2 respectively. BC and DA are the adiabatics.

On the TS diagram the isotherms are two straight lines AB and CD parallel to S-axis and the adiabatic curves are also straight lines BC and DA parallel to T-axis. The resulting TS diagram is a rectangle ABCD.

Consider a Carnot's reversible cycle on TS diagram. Suppose S_1 be the entropy of working substance in state A, S_2 be the entropy in state B. Q_1 be the heat absorbed along AB i.e. isothermal expansion at constant temperature T_1 and Q_2 be the heat rejected in the isothermal compression at constant temperature T_2 along CD.

In going from A to B, along isothermal expansion AB, the gain in entropy of the working substance is given by

$$S_2 - S_1 = \frac{Q_1}{T_1} \quad \dots \dots (1)$$

In going from B to C, along adiabatic expansion BC, there is no change in the entropy.

In going from C to D, along isothermal compression CD, the loss in entropy of the working substance is given by

$$S_2 - S_1 = \frac{Q_2}{T_2} \quad \dots \dots (2)$$

Along the adiabatic compression DA, there is no change in entropy.
From eqs (1) and (2) we get

$$Q_1 = T_1(S_2 - S_1)$$

$$Q_2 = T_2(S_2 - S_1)$$

$$Q_1 - Q_2 = (T_1 - T_2)(S_2 - S_1)$$

and

∴

The quantity $Q_1 - Q_2$ represents the external work done in the cycle and $(T_1 - T_2)(S_2 - S_1)$ is the area of the rectangle on the TS diagram. Thus the area of the rectangle on the TS diagram represents the external work done in a reversible carnot's cycle.

Efficiency of carnot's engine

We have

$$\eta = \frac{Q_1 - Q_2}{Q_1}$$

$$\eta = \frac{(T_1 - T_2)(S_2 - S_1)}{T_1(S_2 - S_1)}$$

$$\therefore \eta = \frac{T_1 - T_2}{T_1} = 1 - \frac{T_2}{T_1}$$

Example 1

Calculate the change in entropy when 100 grams of ice at 0°C is converted into water at the same temperature. Latent heat of ice = 80 cal/g.

Solution

When 1 gram of ice melts into water 80 calories of heat is absorbed.

∴ Heat absorbed by 100 grams of ice when melts = 100×80

i.e.

$$dQ = 8000 \text{ cals}$$

$$\therefore \text{Change in entropy, } dS = \frac{dQ}{T} = \frac{8000}{273}$$

$$= 29.3 \text{ cal/K}$$

Example 2

Calculate the change in entropy when 1 litre of water at 27°C is heated to 77°C .

Solution

Change in entropy $dS = \int_{T_1}^{T_2} \frac{dQ}{T}$

But $dQ = ms \cdot dT = 1000 \times 1 \times dT$

$m = 1000 \text{ g}, \quad T_1 = 27^\circ\text{C} = 300\text{K}$

$s = 1, \quad T_2 = 77^\circ\text{C} = 350\text{K}$

$$\therefore dS = \int_{300}^{350} 1000 \frac{dT}{T} = 1000 \ln\left(\frac{350}{300}\right)$$

$$= 154.15 \text{ cal K}^{-1}$$

Example 3

One mole of a gas expands isothermally to four times its volume. Calculate the change in entropy. $R = 8.31 \text{ J/mol K}$

Solution

$V_1 = V, \quad V_2 = 4V$

Change in entropy, $dS = \frac{dQ}{T}$

During an isothermal process

$$dQ = dW$$

$$dS = \frac{dW}{T}$$

Work done during an isothermal process, $dW = RT \ln\left(\frac{V_2}{V_1}\right)$

$$\therefore dS = \frac{RT \ln\left(\frac{V_2}{V_1}\right)}{T}$$

$$= R \ln\left(\frac{V_2}{V_1}\right) = R \ln 4$$

or

$$\begin{aligned} dS &= \frac{R \ln 4}{4.2} \text{ cal/K} \\ &= \frac{8.31 \times \ln 4}{4.2} = 2.743 \text{ cal/K} \end{aligned}$$

Example 4

Calculate the change in entropy of 5 kg water at 100°C when changes into vapour.
 $L = 540 \text{ cal/g}$

Solution

$$m = 5 \text{ kg} = 5 \times 10^3 \text{ g}, L = 540 \text{ cal/g}, T = 100^\circ\text{C} = 373 \text{ K}$$

$$\begin{aligned} \text{Change in entropy} \quad dS &= \frac{dQ}{T} = \frac{mL}{T} \\ &= \frac{5 \times 10^3 \times 540}{373} = 7.238 \times 10^3 \text{ cal/K} \end{aligned}$$

Example 5

Calculate the change in entropy when 100 gram of water at 30°C is mixed with 50 gram of water at 80°C.

Solution

$$m_1 = 100 \text{ g} \quad T_1 = 303 \text{ K}$$

$$m_2 = 50 \text{ g} \quad T_2 = 353 \text{ K}$$

Let T be temperature after mixing

Using Heat gained = Heat lost

$$m_1 s(T - 303) = m_2 s(353 - T)$$

$$100 \times 1 \times (T - 303) = 50 \times 1 \times (353 - T)$$

$$2(T - 303) = 353 - T$$

$$2T - 606 = 353 - T$$

$$3T = 953$$

$$\therefore T = 319.67 \text{ K}$$

Change in entropy when the temperature of 100 g of water changes from 303 K to 319.67 K

$$dS = \frac{dQ}{T} = ms \int_{T_1}^{T_2} \frac{dT}{T}$$

$$dS_1 = 100 \times 1 \times \ln\left(\frac{319.67}{303}\right)$$

$$= 5.36 \text{ cal/K}$$

The change in entropy when 50 g of water changes 353 K to 319.67 K

$$dS_2 = ms \int_{353}^{319.67} \frac{dT}{T} = ms \ln\left(\frac{319.67}{353}\right)$$

$$dS_2 = 50 \times \ln\left(\frac{353}{319.67}\right) = -4.96 \text{ cal/K} \quad (\because s = 1)$$

\therefore Total gain in entropy

$$= 5.36 - 4.96$$

$$= 0.4 \text{ cal/K}$$

Example 6

Calculate the increase in entropy of 1kg of ice when it is converted into steam. Specific heat of water $1 \text{ k cal kg}^{-1} \text{ C}^{-1}$. Latent heat of ice 80 cal/g and Latent heat of steam 540 cal/g .

Solution

- (a) Increase in entropy when 1 kg of ice at 0°C is converted into water at 0°C

$$dS = \frac{dQ}{T} = \frac{mL}{T} = \frac{1000 \times 80}{273} = 293.04 \text{ cal/K}$$

- (b) Increase in entropy when the temperature of 1 kg of water is raised from 0°C to 100°C .

$$dS = \int_{T_1}^{T_2} \frac{dQ}{T} = \int_{273}^{373} ms \frac{dT}{T} = ms \int_{273}^{373} \frac{dT}{T}$$

$$= 1 \times 10^3 \int_{273}^{373} \frac{dT}{T} = 10^3 \times \ln\left(\frac{373}{273}\right)$$

$$= 312.11 \text{ cal/K}$$

(c) Increase in entropy when 1kg of water at 100°C is converted into steam at 100°C

$$dS = \frac{dQ}{T} = \frac{mL}{T} = \frac{10^3 \times 540}{373}$$

$$= 1447.72 \text{ cal/K}$$

\therefore Total increase in entropy $= 293.04 + 312.11 + 1447.72 = 2052.87 \text{ cal/K}$

Example 7

Calculate the change of entropy on converting a mole of perfect gas occupying 20 litre at a pressure of $2 \times 10^5 \text{ Nm}^{-2}$ to occupying 50 litre at a pressure of $5 \times 10^5 \text{ Nm}^{-2}$. Given $R = 8.4 \text{ J mol}^{-1} \text{ K}^{-1}$, $C_V = 21 \text{ J mol/K}$

Solution

$$P_1 = 2 \times 10^5 \text{ Nm}^{-2}, \quad V_1 = 20 \text{ litre}$$

$$P_2 = 5 \times 10^5 \text{ Nm}^{-2}, \quad V_2 = 50 \text{ litre}$$

Using $\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$

$$\therefore \frac{T_2}{T_1} = \frac{P_2 V_2}{P_1 V_1} = \frac{5 \times 10^5 \times 50}{2 \times 10^5 \times 20} = 6.25$$

$$\text{The change in entropy} = C_V \times \ln\left(\frac{T_2}{T_1}\right) + R \ln\left(\frac{V_2}{V_1}\right)$$

$$= 21 \times \ln(6.25) + 8.4 \ln\left(\frac{5}{2}\right)$$

$$= 46.181 \text{ JK}^{-1}$$

Example 8

A mass m of water at temperature T_1 is isobarically and adiabatically mixed with an equal mass of water at temperature T_2 . Show that the change in entropy of the

universe is $2mC_P \ln\left(\frac{T_1 + T_2}{2\sqrt{T_1 T_2}}\right)$

Solution

When equal amount of water are mixed, the temperature of the mixture is $\frac{T_1 + T_2}{2}$.

Change in entropy of water at temperature T_1

$$dS = \int_{T_1}^{\frac{T_1 + T_2}{2}} \frac{dQ}{T} = m C_P \int_{T_1}^{\frac{T_1 + T_2}{2}} \frac{dT}{T}$$

$$dS = m C_P \ln\left(\frac{T_1 + T_2}{2T_1}\right)$$

Change in entropy of water at temperature T_2

$$\begin{aligned} dS &= \int_{T_2}^{\frac{T_1 + T_2}{2}} \frac{dQ}{T} = m C_P \int_{T_2}^{\frac{T_1 + T_2}{2}} \frac{dT}{T} \\ &= m C_P \ln\left(\frac{T_1 + T_2}{2T_2}\right) \end{aligned}$$

Since the process is adiabatic, change in entropy of the universe

$$= m C_P \ln\left(\frac{T_1 + T_2}{2T_1}\right) + m C_P \ln\left(\frac{T_1 + T_2}{2T_2}\right)$$

$$= m C_P \ln \frac{(T_1 + T_2)^2}{4T_1 T_2}$$

$$= m C_P \ln \left(\frac{T_1 + T_2}{2\sqrt{T_1 T_2}} \right)^2$$

$$= 2m C_p \ln \left(\frac{T_1 + T_2}{2\sqrt{T_1 T_2}} \right)$$

Example 9

Compare the efficiencies of cycles A and B.

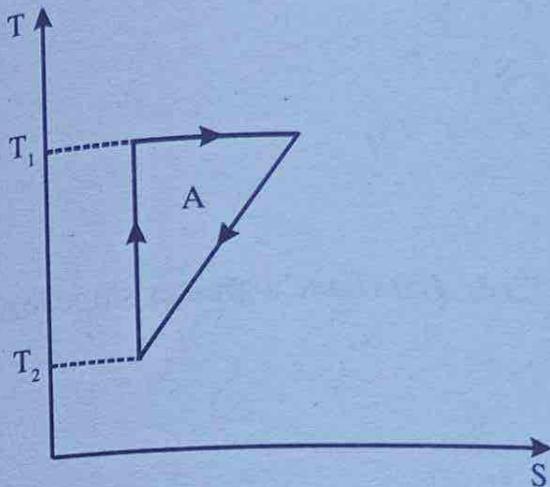


Figure 4.6(a)

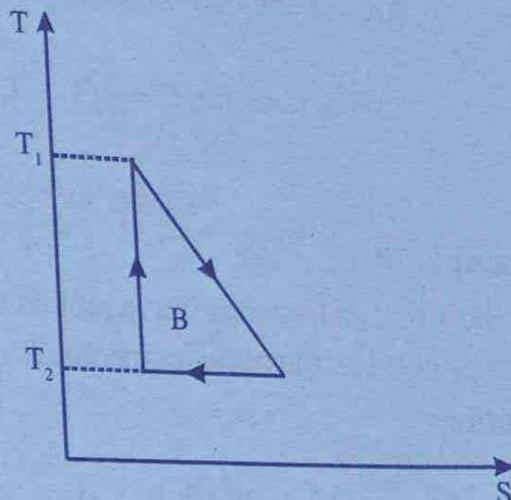


Figure 4.6(b)

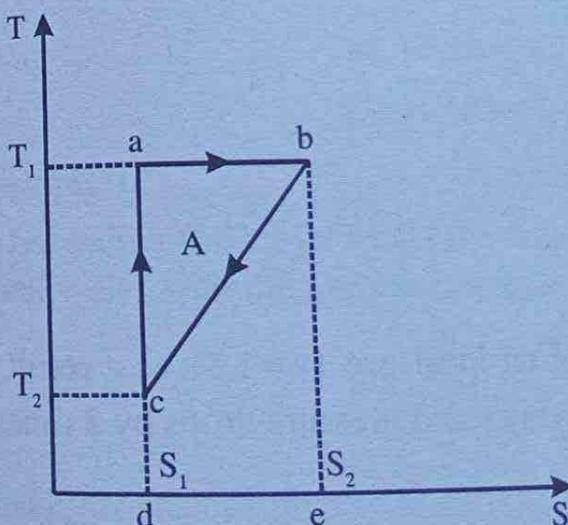
Solution

Figure 4.7(a)

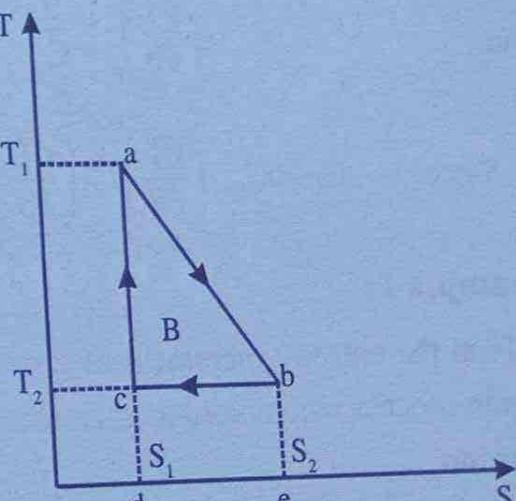


Figure 4.7(b)

Let Q_1 be the amount of heat absorbed during the process in which entropy increases and Q be the amount of heat rejected during the process in which entropy decreases.

$$\eta = \frac{Q_1 - Q_2}{Q_1} = \frac{\text{Area of abc}}{\text{Area of abed}}$$

Area of abc for figure A = Area of abc for figure B.

Area of abed for figure A > Area of abed for figure B

$$\therefore \text{Area of abed for A} = T_1(S_2 - S_1)$$

$$\text{Area of abed for B} = \frac{1}{2}(T_2 - T_1)(S_2 - S_1)$$

$$\therefore \eta_A < \eta_B$$

Example 10

Show that an isochoric curve plotted on a TS diagram have a greater slope than a isobaric curve at the same temperature.

Solution

$$\text{We have } \left(\frac{\partial T}{\partial S} \right)_V = \frac{T}{C_V}$$

$$\text{and } \left(\frac{\partial T}{\partial S} \right)_P = \frac{T}{C_P}$$

$$\text{Since } C_V < C_P, \left(\frac{\partial T}{\partial S} \right)_V > \left(\frac{\partial T}{\partial S} \right)_P$$

Example 11

Find the entropy increment of 2 moles of an ideal gas ($\gamma = 1.3$) as a result of certain process where volume increases by 2 times and pressure drops by 3 times.

Solution

We have

$$dS = C_V \frac{dT}{T} + \frac{PdV}{T}$$

$$dS = C_V \frac{dT}{T} + \frac{nRdV}{V}$$

Integrating,

$$\Delta S = C_V \int_{T_1}^{T_2} \frac{dT}{T} + nR \int_{V_1}^{V_2} \frac{dV}{V}$$

$$\Delta S = C_V \ln \frac{T_2}{T_1} + nR \ln \frac{V_2}{V_1}$$

$$\Delta S = \frac{nR}{\gamma - 1} \ln \frac{T_2}{T_1} + nR \ln \frac{2V_1}{V_1}$$

Using

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$

$$\therefore \frac{T_2}{T_1} = \frac{P_2}{P_1} \frac{V_2}{V_1} = \frac{1}{3} \cdot 2 = \frac{2}{3}$$

$$\therefore \Delta S = \frac{2R}{1.3 - 1} \ln \frac{2}{3} + 2R \ln 2$$

$$\Delta S = \frac{2 \times 8.31}{0.3} \ln \frac{2}{3} + 2 \times 8.31 \times \ln 2$$

$$\Delta S = -22.46 + 11.52$$

$$\Delta S = -10.94 \text{ J}$$

Example 12

According to Debye's law, the molar heat capacity at constant volume of a diamond varies with the temperature as

$$C_V = 3R \frac{4\pi^4}{5} \left(\frac{T}{\Theta} \right)$$

what is the entropy change in units of R of a diamond of 1.2 g mass when it is heated at constant volume from 10 to 350 K. The molar mass of diamond is 12 g and Θ is 2230 K.

Solution

We have

$$\Delta S = n \int C_V \frac{dT}{T} + nR \int \frac{dV}{V}$$

since volume is kept constant $dV = 0$

$$\Delta S = n \int_{10}^{350} C_V \frac{dT}{T}$$

$$n = \frac{1.2}{12} = 0.10$$

$$\Delta S = 0.10 \int_{10}^{350} 3R \frac{4\pi^4}{5} \frac{T^3}{\Theta^3} \frac{dT}{T}$$

$$\Delta S = \frac{0.10 \times 12\pi^4}{5\Theta^3} R \int_{10}^{350} T^2 dT$$

$$\Delta S = \frac{2.4\pi^4 R}{\Theta^3} \left[\frac{T^3}{3} \right]_{10}^{350}$$

$$\Delta S = \frac{0.8\pi^4 R}{\Theta^3} (350^3 - 10^3)$$

$$\Delta S = \frac{0.8\pi^4 R}{2230^3} (350^3 - 10^3)$$

$$\Delta S = \frac{0.8\pi^4 R (42875000 - 1000)}{2230^3}$$

$$\Delta S = 0.3006 R$$

Entropy and reversibility

When a system undergoes an entropy change, it may absorb heat from the surroundings or reject heat to the surroundings. Thus in order to understand the entropy change it is necessary to learn the entropy change of the system as well as that of the surroundings. Then only the study will be completed. If ΔS_1 be the entropy change of the system and ΔS_2 be that of surroundings, then $\Delta S_1 + \Delta S_2$ is known as the entropy change of the universe.

Suppose a system is in contact with a reservoir. The system may absorb heat or

reject to the reservoir. Though the reservoir can absorb or reject any amount of heat without change of its temperature it is due to the flow of heat in or out of the reservoir, entropy change is accompanied. If Q be the amount of heat absorbed by the reservoir at constant temperature T , then the entropy change of the reservoir is $+\frac{Q}{T}$.

If the heat flows out of the reservoir, the entropy change is $-\frac{Q}{T}$.

Now consider a reversible process in which dQ_R be the amount of heat transferred to the reservoir at temperature T .

Then

$$\text{change in entropy of the system} = -\frac{dQ_R}{T}$$

$$\text{change in entropy of the reservoir} = +\frac{dQ_R}{T}$$

$$\therefore \text{Entropy change of the reservoir} = -\frac{dQ_R}{T} + \frac{dQ_R}{T} = 0$$

If dQ_R be the amount of heat rejected by the reservoir at constant temperature T ,

then

$$\text{entropy change of the system} = -\frac{dQ_R}{T}$$

$$\text{entropy change of the reservoir} = +\frac{dQ_R}{T}$$

$$\therefore \text{Total entropy change of the universe} = \frac{dQ_R}{T} - \frac{dQ_R}{T} = 0$$

It shows that **for a reversible process the total change in entropy of the universe is zero.**

Remember that all natural processes are irreversible and only ideal processes are reversible.

Note: It may be noted that when heat is absorbed entropy change is positive.

Example 13

Calculate the entropy change of the universe as a result of

- a) A copper block of 0.4 kg mass and with heat capacity at constant pressure of 150 JK^{-1} at 100°C is placed in a lake at 10°C
- b) The same block at 10°C is dropped from a height of 100 m into the lake.
- c) Two such blocks at 100°C and 10°C are joined together.

Solution

a) Entropy

$$dS = \frac{dQ}{T} = C_p \frac{dT}{T}$$

change of entropy of copper $\Delta S_1 = \int_{373}^{283} C_p \frac{dT}{T} = C_p \ln \frac{283}{373}$

$$\Delta S_1 = 150 \times \ln \frac{283}{373} = -41.42 \text{ JK}^{-1}$$

change of entropy of the reservoir (lake)

$$\Delta S_2 = \frac{Q}{T} = \frac{mc_p(T_f - T_i)}{T_i}$$

$$\Delta S_2 = \frac{150(373 - 283)}{283} = 47.70$$

$$mc_p = C_p.$$

$$\therefore \text{Entropy change of the universe} = \Delta S_1 + \Delta S_2 = 6.28 \text{ JK}^{-1}$$

b) Work done when it touches water = mgh

$$W = 0.4 \times 9.8 \times 100 = 392 \text{ J}$$

$$(\Delta S)_{cu} = 0$$

$$(\Delta S)_{lake} = \frac{W}{T} = \frac{392}{283} = 1.385 \text{ JK}^{-1}$$

$$\therefore (\Delta S)_{universe} = (\Delta S)_{cu} + (\Delta S)_{lake} = 1.385 \text{ JK}^{-1}$$

c) Final temperature of the block $= \frac{373 + 273}{2} = 323 \text{ K}$

$$(\Delta S)_I = C_p \int_{373}^{323} \frac{dT}{T} = 150 \ln \frac{323}{373} = -21.59 \text{ JK}^{-1}$$

$$(\Delta S)_{II} = C_p \int_{273}^{323} \frac{dT}{T} = 150 \ln \frac{323}{273} = 25.23 \text{ JK}^{-1}$$

$$(\Delta S)_{\text{universe}} = (\Delta S)_I + (\Delta S)_{II} = 3.64 \text{ JK}^{-1}$$

Entropy and irreversibility

When a system undergoes an irreversible process the entropy change of the universe is entirely different. Suppose a system undergoes an irreversible process from an equilibrium state A to another equilibrium state B the change in entropy is

$$S_B - S_A = \int_A^B \frac{dQ}{T}$$

since the process is irreversible the path of integration is not known. Thus integration cannot be performed. Then what we do is as the initial and final states are in equilibrium, choose an arbitrary path and perform the integration without changing the initial and final equilibrium states. This gives the entropy change of an irreversible process

$$\text{i.e. } S_B - S_A = \int_{RA}^B \frac{dQ}{T} \quad \dots \dots (21)$$

If the initial and final states are not in equilibrium some special methods are used. Depending upon the process of irreversibility, calculations are different.

1. External mechanical irreversibility processes

- a) Processes involving the isothermal dissipation of work through a system (remains unchanged) into internal energy of a reservoir is called external mechanical irreversibility processes.

Examples

- (i) Friction from two solids in contact with a reservoir.
- (ii) Irregular stirring of a viscous liquid in contact with a reservoir.
- (iii) Transfer of charge through a resistor in contact with a reservoir.
- (iv) Magnetic hysteresis of a material in contact with a reservoir.

Calculation of entropy

According to first law, during an isothermal process $Q = W$.
i.e. Q be the amount of heat flows into the reservoir.

$$\therefore \text{Entropy change of the reservoir} = \frac{Q}{T} = \frac{W}{T} \quad \dots \dots (22)$$

As the system remains unchanged the entropy change of the universe is equal to entropy change of the reservoir, which is $\frac{Q}{T}$. As it is positive quantity entropy of the universe increases.

- b) Now we consider processes involving the adiabatic dissipation of work into the internal energy of a system open to the atmosphere.

Examples

- (i) Friction from rubbing thermally insulated liquids
- (ii) Irregular stirring of a viscous liquid inside thermally insulated walls.
- (iii) Transfer of charge through a thermally insulated resistor.
- (iv) Magnetic hysteresis of a thermally insulated material

Calculation of entropy change

As the process is adiabatic $dQ = 0$. Here work goes over into internal energy of the system, whose temperature rises from T_A to T_B at constant atmospheric pressure. As there is no heat transfer to or from the surroundings, there is no change in entropy of the surroundings. To calculate the entropy change of the system, the original irreversible path is replaced by a reversible path without changing the initial equilibrium state (P, T_A) and the final equilibrium state (P, T_B).

\therefore The entropy change of the system

$$S_B - S_A = \int_{RT_A}^{T_B} \frac{dQ}{T}$$

For an isobaric process $dQ = C_p dT$

$$S_B - S_A = \int_{T_A}^{T_B} C_p \frac{dT}{T}$$

If C_p is constant

$$S_B - S_A = C_p \ln \frac{T_B}{T_A} \quad \dots\dots (23)$$

Thus, the entropy change of the universe is same as the entropy change of the system. This is a positive quantity.

2. Internal mechanical irreversibility processes

When a system undergoes a process in which the internal energy of a system enclosed by adiabatic walls transformed into mechanical energy and then back into internal energy is called internal mechanical irreversibility process.

Examples

- (i) Ideal gas rushing into vacuum (free expansion)
- (ii) Gas flowing through a porous plug (Throttling process)
- (iii) Collapse of a soap film after it is punctured.

Calculation of entropy change

As the system is enclosed by adiabatic walls there is no heat transfer into or from the surroundings. Thus the entropy change of the surroundings is zero. To calculate the entropy change of this irreversible system the process is replaced by a reversible path without changing the initial equilibrium state (V_A, T) and the final equilibrium state (V_B, T) of the irreversible process.

\therefore The change in entropy of the system is

$$S_B - S_A = \int_{V_A}^{V_B} \frac{dQ_R}{T}$$

For an isothermal process

$$dQ_R = PdV$$

$$\text{or } \frac{dQ_R}{T} = \frac{PdV}{T} = nR \frac{dV}{V}$$

$$\therefore S_B - S_A = \int_{V_A}^{V_B} nR \frac{dV}{V}$$

$$S_B - S_A = nR \ln \frac{V_B}{V_A} \quad \dots\dots (24)$$

Thus the entropy change of the universe is $nR \ln \frac{V_B}{V_A}$. This is again a positive quantity.

3. External thermal irreversibility processes

A process in which heat transfers from the system to surroundings or vice versa by virtue of a finite temperature difference is called as external thermal irreversibility process

Examples

- Conduction or radiation of heat from a system to its cooler surroundings.
- Conduction or radiation of heat through a system (which remains unchanged) from a hot reservoir to a cooler one.

Calculation of entropy change

Let Q be the amount of heat transferred from one end to the other end of the system (remains unchanged) from a hot reservoir at temperature T_1 , a cooler reservoir at temperature T_2 .

$$S_B - S_A \text{ of the system} = 0$$

$$S_B - S_A \text{ of the hotter reservoir} = -\frac{Q}{T_1}$$

$$S_B - S_A \text{ of the cooler reservoir} = +\frac{Q}{T_2}$$

$$\therefore S_B - S_A \text{ of the universe} = \frac{Q}{T_2} - \frac{Q}{T_1} \quad \dots\dots (25)$$

Here again the entropy change of the universe is positive since $T_1 > T_2$.

Chemical irreversibility processes

Processes involving a spontaneous change of internal structure, density, chemical composition etc. are called chemical irreversibility processes.

Examples

- Diffusion of two dissimilar inert ideal gases.
- Mixing of alcohol and water
- Osmosis

- (iv) Dissolution of solid in water
 (v) A chemical reaction.

Calculation of entropy change

Consider mixing of two inert gases initially in separate adiabatic enclosures with equal volume V . Let A be the initial equilibrium state of the system. When they are allowed to mix they come to another equilibrium state B. While mixing this can be considered as two separate free expansions in an adiabatic enclosure.

The change entropy one gas is

$$S_B - S_A = nR \ln \frac{V_B}{V_A} \quad (\text{equation 24})$$

The change in entropy of the second gas is

$$S_B - S_A = nR \ln \frac{V_B}{V_A}$$

Entropy change of the universe due to irreversible processes

Type of irreversibility	Irreversible process	Entropy change of the system	Entropy change of the local surroundings	Entropy change of the universe
External mechanical irreversibility	Isothermal dissipation of work through a system into internal through a system into internal energy of a reservoir.	0	$\frac{W}{T}$	$\frac{W}{T}$
	Adiabatic dissipation of work into internal energy of a system.	$C_p \ln \frac{T_f}{T_i}$	0	$C_p \ln \frac{T_f}{T_i}$
Internal mechanical irreversibility	Free expansion of an ideal gas.	$nR \ln \frac{V_f}{V_i}$	0	$nR \ln \frac{V_f}{V_i}$
External thermal irreversibility	Transfer of heat through a medium from a hotter to a cooler reservoir.	0	$\frac{Q}{T} - \frac{Q}{T_i}$	$\frac{Q}{T_2} - \frac{Q}{T_1}$
Chemical irreversibility	Diffusion of two dissimilar inert ideal gases.	$2nR \ln \frac{V_f}{V_i}$	0	$2nR \ln \frac{V_f}{V_i}$

∴ change in entropy of the system (two gases) is

$$S_B - S_A = 2nR \ln \frac{V_B}{V_A} \quad \dots\dots (26)$$

Since there is no change of entropy of the reservoir, the entropy change of the universe $= 2nR \ln \frac{V_B}{V_i}$, which is positive.

In general we can say that for any irreversible process the change of entropy is positive. i.e., for all irreversible processes the entropy of the universe increase.

Irreversible part of the second law

The irreversible part of the second law leads to Clausius' inequality or Clausius' inequality is the mathematical statement of the irreversible part of second law.

Clausius inequality theorem states that for any closed irreversible process

$$\oint \frac{dQ}{T} < 0$$

Proof

Consider a heat reservoir (source) at temperature T_1 supplying a small quantity of heat dQ_1 to a reversible engine R. The purpose of R is to provide heat for the irreversible engine I. Engine R rejects a small amount of heat dQ_2 at temperature T_2 that is supplied to the irreversible engine I. Engine I does a small amount of work dW during an irreversible cycle, so the combined system of engine R and engine I also performs as an irreversible cycle. The net work of the combined system, according to the first law, equals

$\oint dQ_1$. But the net work cannot be positive according to the Kelvin-Planck statement of the second law, since the combined system exchanges heat with a single reservoir. So $\oint dQ_1$

cannot be positive. Moreover if $\oint dQ_1$ equals zero, then at the end of the cycle, engine I and its surroundings have returned to their

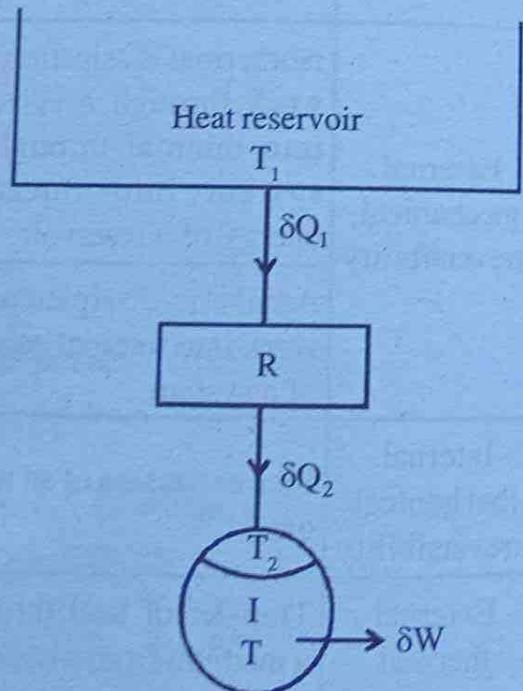


Figure 4.8

original state. This result is contrary to the irreversibility of engine I. So we conclude that

$$\oint dQ_1 < 0 \quad \dots\dots (1)$$

For the reversible engine R, we have

$$\frac{dQ_1}{T_1} = -\frac{dQ_2}{T_2}$$

Integrating around a closed cycle, we get

$$\oint \frac{dQ_1}{T_1} = - \oint \frac{dQ_2}{T_2}$$

Since T_1 is constant (reservoir temperature)

$$\frac{1}{T_1} \oint_R dQ_1 = - \oint_R \frac{dQ_2}{T_2} \quad \dots\dots (2)$$

The heat dQ_2 rejected from R is absorbed by I, we can write

$$(dQ_2)_R = -(dQ_2)_I$$

When this is substituted in eqn 2 on the right hand side, we get

$$\frac{1}{T_1} \oint_R dQ_1 = \oint_I \frac{dQ_2}{T_2}$$

$$\text{or} \quad T_1 \oint_I \frac{dQ_2}{T_2} = \oint_R dQ_1$$

But $\oint_R dQ_1 < 0$ see eqn 1.

$$T_1 \oint_I \frac{dQ_2}{T_2} < 0$$

\therefore Since $T_1 > 0$, we have

$$\oint_I \frac{dQ_2}{T_2} < 0$$

If dQ is the heat absorbed by the irreversible engine at temperature T , we can write

$$\oint_I \frac{dQ}{T} < 0 \quad \dots\dots (3)$$

This is known as clausius inequality.

Clausius' mathematical statement of second law

For a reversible process, we have

$$\oint_R \frac{dQ}{T} = 0 \quad \dots\dots (4)$$

For an irreversible process, we have

$$\oint_I \frac{dQ}{T} < 0 \quad \dots\dots (5)$$

Combining eqns 4 and 5, we get

$$\oint \frac{dQ}{T} \leq 0 \quad \dots\dots (6)$$

Remember that equality sign is for reversible process and inequality sign is for irreversible process. Equation 6 is the *clausius mathematical statement of second law*.

Heat and entropy in irreversible processes

Consider a system under goes an irreversible process (I) from an initial equilibrium state A to final equilibrium state B. The system comes back to initial equilibrium position by a reversible process (R) as shown in figure below.

The entropy of a closed system is

$$\oint dS = \int_A^B dS + \int_R^B dS \quad \dots\dots (27)$$

since entropy is a state function

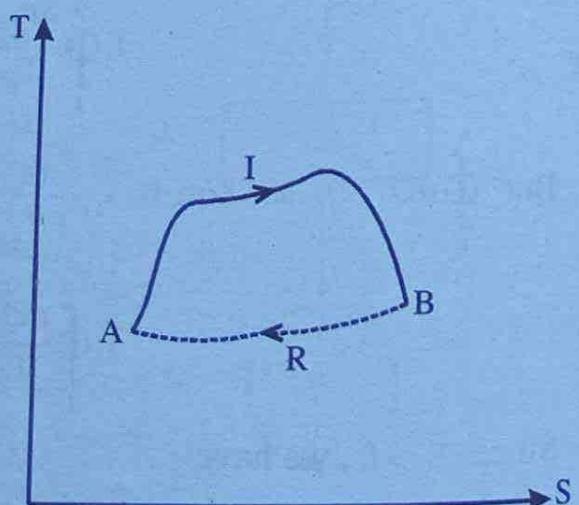


Figure 4.9

$$\oint dS = 0.$$

$$0 = \int_A^B dS + \int_R^A dS$$

i.e.

$$-\int_R^B dS = \int_A^B dS$$

$$\int_R^B dS = \int_A^B dS$$

or

But from Clausius's inequality theorem we have

$$\oint_I \frac{dQ}{T} = \int_A^B \frac{dQ}{T} + \int_R^A \frac{dQ}{T} < 0 \quad \dots\dots (28)$$

From the definition of entropy

$$\int_R^B \frac{dQ}{T} = \int_R^A dS$$

i.e.,

$$\oint_I \frac{dQ}{T} = \int_A^B \frac{dQ}{T} + \int_R^A dS < 0 \quad \dots\dots (29)$$

i.e.,

$$\int_A^B \frac{dQ}{T} + \int_R^B dS < 0$$

or

$$\int_A^B \frac{dQ}{T} - \int_A^B dS < 0 \quad \left(\because \int_R^A dS = \int_B^A dS \right)$$

or

$$\int_A^B dS - \int_A^B \frac{dQ}{T} > 0$$

$$\int_A^B dS > \int_A^B \frac{dQ}{T}$$

This shows that the change of entropy during irreversible process is greater than the integral of the heat divided by temperature of the reservoir. For infinitesimal changes in state the above inequality can be written as

$$dS_I > \left(\frac{dQ}{T} \right)_I$$

For reversible process, we have

$$dS_R = \left(\frac{dQ}{T} \right)_R$$

combining the two we can write

$$dS \geq \frac{dQ}{T} \quad \dots\dots (30)$$

while dealing with entropy we should be careful about whether it is reversible or irreversible.

According to the definition of entropy

$$dS = \frac{dQ_R}{T}$$

For a reversible adiabatic process $dQ_R = 0$ implies $dS = 0$.

$dS = 0$ means that entropy is constant thus we call this as isentropic.

Suppose we consider an irreversible isentropic process. Obviously $dS = 0$, but

$$\frac{dQ}{T} < 0$$

i.e. $dQ < 0$ so not adiabatic.

In general isentropy does not mean that it is adiabatic. Only reversible isentropic implies adiabatic. Irreversible isentropic implies not adiabatic.

Principle of increase of entropy

We calculated the change in entropy of universe for several irreversible processes. In all processes it is seen that the entropy of the universe increases. This is known as the entropy principle. Now we want to establish this statement. For this we consider a cyclic process in which a system undergoes an irreversible adiabatic process, a reversible adiabatic process, reversible isothermal process and a reversible adiabatic process and finally comes back to the initial state. These processes are depicted in a work diagram as shown 4.10.

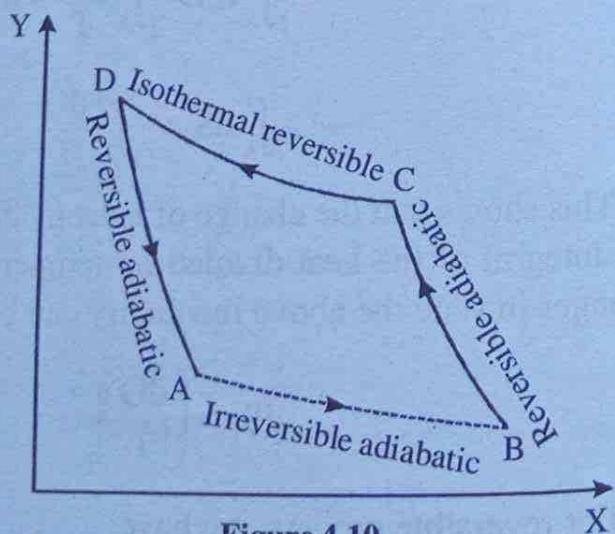


Figure 4.10

Let A be the initial state of the system. Suppose the system undergoes an irreversible adiabatic process to the state B. Then the change in entropy is

$$\Delta S = S_B - S_A \quad \dots \dots (31)$$

The temperature of the system may or may not change.

Now let the system undergo a reversible adiabatic process to the state C in such a way that temperature changes infinitesimally through a sequence of process finally attaining a temperature T' of an arbitrarily chosen reservoir. Since B and C are at the same adiabatic points we can very well write

$$S_B = S_C$$

Thus equation 31, becomes

$$\Delta S = S_C - S_A \quad \dots \dots (32)$$

Now the system is at C in contact with the reservoir at T' , the system at C is allowed to undergo a reversible isothermal process until the system attains an entropy same as in the state A. The system is now at the state D having the same entropy of the system at A.

$$S_D = S_A$$

i.e.

The equation 32 now becomes

$$\Delta S = S_C - S_D \quad \dots \dots (33)$$

Finally the system at D is allowed to undergo a reversible adiabatic process to arrive at the initial state A.

In the entire cyclic process heat transfer occur only during the reversible isothermal process ($C \rightarrow D$). the heat transferred

$$Q_R = T'(S_D - S_C) \quad \dots \dots (34)$$

The net work done in the cycle is

$$W = Q_R$$

According to second law of thermodynamics Q_R cannot be positive that is heat cannot have entered the system, for then we would have a cyclic process where the only effect would be the absorption of heat from a single reservoir and the performance of an equivalent amount of work.

\therefore

$$Q_R \leq 0$$

Putting this in equation 34

$$T'(S_D - S_C) \leq 0$$

or

$$T'(S_C - S_D) \geq 0$$

since $T' \geq 0$

$$S_C - S_D \geq 0$$

or

$$\Delta S \geq 0.$$

If we assume that the original irreversible adiabatic process would have occurred without any change in entropy, then it would be to bring the system back to the initial position by means of one reversible adiabatic process. Moreover since the net heat transferred in this cycle is zero, no work would be done. Therefore under these circumstances the system its surroundings would have been restored without producing any changes, which implies that the original process was reversible. Since this is contrary to our assumption that the process was irreversible, the entropy of the system cannot remain unchanged

$$\therefore \Delta S > 0.$$

Since entropy could not have decreased.

Application of entropy principle

According to the entropy principle for all irreversible processes entropy of the universe increases. When applying this principle to machines such as engines or refrigerator we can gather information regarding the behaviour of the machine.

For example consider a refrigerator operating between temperature T_1 and T_2 . Suppose a quantity of heat Q is removed from an object inside the refrigerator by doing W amount of work. Then the body goes from its initial state to final state B.

$$\Delta S \text{ of the body} = S_B - S_A$$

$$\Delta S \text{ of the refrigerant} = 0$$

$$\Delta S \text{ of the reservoir} = \frac{Q + W}{T_1}$$

Since $Q + W$ amount of the heat is rejected to the reservoir.

Applying the entropy principle

$$\Delta S \geq 0, \text{ we get}$$

$$S_B - S_A + \frac{Q+W}{T_1} \geq 0$$

Multiplying T_1 yields.

$$T_1(S_B - S_A) + Q + W \geq 0$$

$$W \geq T_1(S_A - S_B) - Q$$

or

$$(W)_{\min} = T_1(S_A - S_B) - Q$$

Knowing T_1 , S_A , S_B and Q , the minimum work required to be calculated. It provides us an estimate of the minimum cost of operation of the refrigerator.

Entropy and disorder

We know that all natural processes are irreversible. For all irreversible processes entropy increase. This is because when a system undergoes an irreversible process, the order of the final state is less than the order of the initial state. In other words, when the disorder increases entropy increases. That is an increase of entropy of a system can be described as an increase in the disorder of the system. Now we will see that how entropy is connected with disorder by taking several examples of irreversible processes.

Examples

- Consider a solid in its initial state. The particles which are the constituents of the solid are in infinite order. When the solid is allowed to undergo an irreversible process by supplying heat to it sublimation occurs. During sublimation there is no change in temperature at the same time system absorbs heat (Q). The entropy

change can be calculated by $\frac{Q}{T}$, which is positive. We can say that entropy

increases. The final state of the solid is obviously vapour. The particles which are the constituents of vapour occupy greater volume and particles are in random motion. So the final state is disordered than the initial state.

- Consider the case of isothermal expansion of an ideal gas. As the gas absorbs heat it expands slowly. At the end of the process the gas occupies a larger volume. The gas molecules are more disordered now. We say that the entropy of the gas has increased because the amount of disorder has increased. At the same time we already proved that during isothermal expansion the entropy increases.

3. Now we consider a ferromagnetic material, its magnetic dipole moments are mostly aligned in one direction i.e., initially ferromagnetic material is in ordered state. When the material is heated to a temperature above Curie temperature phase change occurs and it is an irreversible process. The system now attains another state exhibiting the behaviour of paramagnetic material in which magnetic dipole moments are randomly oriented (disordered). It is due to this behaviour entropy of the system increases.

The above discussions show that entropy of a system and its surroundings will always increase during irreversible processes. i.e., entropy of an irreversible process move always forward. Metamorphically we say entropy is the arrow of time.

Exact differentials

According to first law of thermodynamics

$$dQ = dU + dW$$

or

$$dU = dQ - dW$$

on the L.H.S we have an exact differential. On the R.H.S both are inexact differentials. Then how it is consistent. In mathematics there is a technique of converting inexact differential into exact differential by multiply with an integrating factor. The same technique is followed in thermodynamics. We defined work done as

$$dW = PdV$$

or

$$\frac{dW}{P} = dV$$

Here dW is inexact, by multiply with an integrating factor it becomes an exact differential dV . Or writing

$$dW = PdV$$

it becomes an exact differential. Remember that only for quasistatic infinitesimal process it is valid.

Similarly the inexact differential dQ can be converted into exact differential with the help of definition of entropy, we have

$$dS = \frac{dQ}{T}$$

Here dS is an exact differential as it is a state function. However, dQ is inexact since it depends on path. The definition of temperature enables us to convert inexact

differential dQ into an exact differential by multiplying with an integrating factor

$$\frac{1}{T}$$

$$dQ = TdS$$

or

The first law of thermodynamics can be rewritten as

$$dU = TdS - PdV$$

Now both sides are exact differentials.

Note : While writing the first law of thermodynamics we didn't use sign convention.
Even if use sign convention nothing happens to final equation.

IMPORTANT FORMULAE

1. For any reversible cycle: $\oint \frac{dQ_R}{T} = 0$

2. Change in entropy: $S_B - S_A = \int_A^B \frac{dQ}{T}$

or $dS = \frac{dQ_R}{T}$

3. Entropy of the ideal gas.

(i) In terms of T and V

$$\frac{dQ}{T} = C_v \frac{dT}{T} + nR \frac{dV}{V}$$

or

$$S = C_v \ln T + nR \ln V + S_0$$

(ii) In terms of T and P

$$\frac{dQ_R}{T} = C_p \frac{dT}{T} - nR \frac{dP}{P}$$

or

$$S = C_p \ln T - nR \ln P + S_0$$

(iii) In terms of P and V

$$\frac{dQ_R}{T} = C_p \frac{dV}{V} + C_v \frac{dP}{P}$$

or

$$S = C_p \ln V + C_v \ln P + S_0$$

4. In TS diagram slopes are

$$(i) \left(\frac{\partial T}{\partial S} \right)_P = \frac{T}{C_P}$$

$$(ii) \left(\frac{\partial T}{\partial S} \right)_V = \frac{T}{C_V}$$

$$\left(\frac{\partial T}{\partial S} \right)_V > \left(\frac{\partial T}{\partial S} \right)_P$$

5. Entropy of reversible processes

(i) Change in entropy of a Carnot cycle

$$\frac{Q_1}{T_1} + \frac{Q_2}{T_2} = 0.$$

(ii) Total entropy change of the universe = 0.

6. Entropy and irreversibility.

(i) The entropy change,

$$S_B - S_A = \int_A^B \frac{dQ}{T}$$

(This integral cannot be calculated)

(ii) Entropy change in external mechanical irreversibility process.

(a) Isothermal dissipation of work through the system into internal energy of the reservoir.

Entropy change of the system = 0

$$\text{Entropy change of the surroundings} = \frac{W}{T}$$

$$\text{Entropy change of the universe} = \frac{W}{T}.$$

(b) Adiabatic dissipation of work into internal energy of the system.

$$\text{Entropy change of the system} = C_P \ln \frac{T_B}{T_A}$$

Entropy change of the surroundings = 0

$$\text{Entropy change of the universe} = C_P \ln \frac{T_B}{T_A}.$$

- (iii) Entropy change in internal mechanical irreversibility process.
 (a) Free expansion of ideal gas.

$$\text{Entropy change of the system} = nR \ln \frac{V_B}{V_A}$$

$$\text{Entropy change of the surroundings} = 0$$

$$\text{Entropy change of the universe} = nR \ln \frac{V_B}{V_A}$$

- (iv) Entropy change in external thermal irreversibility process.

- (a) Transfer of heat through a medium from a hotter to a cooler reservoir.
 Entropy change of the system = 0

$$\text{Entropy change of the surroundings} = \frac{Q}{T_B} - \frac{Q}{T_A}$$

$$\text{Entropy change of the universe} = \frac{Q}{T_B} - \frac{Q}{T_A}$$

- (v) Entropy change in chemical irreversibility process.

- (a) Diffusion of two dissimilar inert ideal gases.

$$\text{Entropy change of the system} = 2nR \ln \frac{V_B}{V_A}$$

$$\text{Entropy change of the surroundings} = 0$$

$$\text{Entropy change of the universe} = 2nR \ln \frac{V_B}{V_A}$$

7. Clausius' theorem: $\oint \frac{dQ}{T} \leq 0$

8. Change in entropy of ice at 0°C is converted into steam

$$\Delta S = \frac{mL_{ice}}{T_{ice}} + mC \int_{273}^{373} \frac{dT}{T} + \frac{mL_{steam}}{T_{steam}}$$

$$L_{ice} = 336 \times 10^3 \text{ J kg}^{-1}$$

$$L_{steam} = 2268 \times 10^3 \text{ J kg}^{-1}$$

C = specific heat of water

$$= 4200 \text{ J kg}^{-1} \text{ K}^{-1}$$

9. When equal amount of water at one at temperature T_1 the other at temperature T_2 are mixed adiabatically and isobarically

$$(\Delta S_3)_I = \int_{T_1}^{T_f} \frac{dQ}{T}, \quad (\Delta S)_{II} = \int_{T_2}^{T_f} \frac{dQ}{T}$$

where $T_f = \frac{T_1 + T_2}{2}$ and $dQ = C_p dT$

$$\Delta S = (\Delta S)_I + (\Delta S)_{II}$$

10. When two different liquids of masses m_1 and m_2 , specific heats c_1 and c_2 and temperatures T_1 and T_2 respectively are mixed.

Final temperature

$$T_f = \frac{m_1 c_1 T_1 + m_2 c_2 T_2}{m_1 c_1 + m_2 c_2}$$

$$(\Delta S)_I = \int_{T_1}^{T_f} \frac{m_1 c_1 dT}{T}, \quad (\Delta S)_{II} = \int_{T_2}^{T_f} \frac{m_2 c_2 dT}{T}$$

Total change in entropy

$$\Delta S = (\Delta S)_I + (\Delta S)_{II}$$

UNIVERSITY MODEL QUESTIONS

Section A

(Answer questions in about two or three sentences)

Short answer type questions

1. What is work diagram?
2. State Clausius' theorem for a reversible process.
3. Define entropy. What is its unit?
4. Express entropy change of ideal gas in terms of temperature and pressure.
5. Express entropy change of ideal gas in terms of pressure and temperature.
6. Express entropy change of ideal gas in terms of pressure and volume.
7. What enables us to draw TS diagram?
8. What is a TS diagram?
9. What are the advantages of TS diagram over PV diagram?
10. Draw a TS diagram for a Carnot cycle.

11. Show that entropy is a constant for a reversible adiabatic process.
12. Show that $\left(\frac{\partial T}{\partial S}\right)_P = \frac{T}{C_P}$.
13. Show that $\left(\frac{\partial T}{\partial S}\right)_V = \frac{T}{C_V}$.
14. Draw isochoric and isobaric curve on a TS diagram.
15. What is meant by entropy change of the universe?
16. Mention four types of irreversibility processes.
17. What is external mechanical irreversibility process?
18. Give two examples of external mechanical irreversibility process.
19. Define internal mechanical irreversible process.
20. Give two examples for internal mechanical irreversibility process.
21. What is meant by chemical irreversibility process?
22. Give two examples of chemical irreversible process.
23. When a system is said to undergo thermal irreversible process?
24. Give two examples of thermal irreversible process.
25. State Clausius' theorem.
26. Write down the Clausius mathematical statement of second law and explain the symbols.
27. In general isentropic does not mean that adiabatic. Justify.
28. Distinguish between isentropic process and adiabatic process.
29. What is meant by entropy principle?
30. What is the relation between entropy and disorder?
31. How will you convert an inexact differential into exact differential?

Section B

(Answer questions in a paragraph of about half a page to one page)

Paragraph / Problem type questions

1. For a reversible process show that heat transferred in an isothermal process can be made equal to that in an adiabatic-isothermal-adiabatic process.
2. Prove Clausius' theorem for a reversible cyclic process.
3. Prove that entropy is a state function.
4. Show that for a Carnot cycle entropy remains constant.
5. Derive an expression for the entropy of ideal gas in terms of temperature and volume.
6. Derive an expression for the entropy of ideal gas in terms of pressure and temperature.

7. Derive an expression for the entropy of ideal gas in terms of pressure and volume.
8. Define entropy. What is its unit?
9. Derive an expression for entropy.
10. Show that during an adiabatic process entropy remains constant.
11. A current of 10A is maintained for 1s in a resistor of 25Ω while the temperature of resistor is kept constant. What is the entropy change of the universe. $[8.33\text{JK}^{-1}]$
12. One kilogram of water at 273K is brought into contact with a heat reservoir at 373K . When the water has reached 373K , what is the entropy change of the water, of the heat reservoir and of the universe. $[1311\text{JK}^{-1}, -1126\text{JK}^{-1}, 185\text{JK}^{-1}]$
13. A $1\mu\text{F}$ capacitor is connected to a 100V electrochemical cell at 0°C . Calculate the change in entropy. $[1.83 \times 10^{-5}\text{JK}^{-1}]$
14. Show that an isochoric curve plotted on a T-S diagram have a greater slope than an isobaric curve at the same temperature.
15. Calculate the change in entropy of the universe if a quantity of 100kJ is transferred from a reservoir at 553K to another reservoir at 278K . $[1.449 \times 10^3\text{JK}^{-1}]$
16. Show that area of the rectangle of a TS diagram of a Carnot cycle gives the work done.
17. Derive an expression for efficiency from TS diagram of a Carnot engine.
18. Show that for a reversible process the total change in entropy of the universe is zero.
19. How to calculate the entropy change of an irreversible process?
20. Calculate the change in entropy of the universe when a system undergoes external mechanical irreversible process.
21. Calculate the change in entropy of the universe when a system undergoes internal mechanical irreversible process.
22. Calculate the change in entropy of the universe when a system undergoes external thermal irreversibility process.
23. Calculate the change in entropy of the universe when a system undergoes chemical irreversible process.
24. Prove Clausius' inequality theorem.
25. Show that $dS \geq \frac{dQ}{T}$
26. Applying the entropy principle to a refrigerator calculate the minimum amount of work required to be done.
27. An increase of entropy of a system can be described as an increase in the disorder of the system. Justify.

Section C
(Answer questions in about two pages)

Long answer type questions (Essays)

1. State and prove Clausius theorem for entropy and write down Clausius mathematical statement of second law.
2. Derive the expression for the change in entropy of perfect gas in terms of
 (i) T and V (ii) T and P (iii) P and V.

Hints to problems

8. See example 1
9. See example 2

10. $dS = C_V \ln\left(\frac{T_2}{T_1}\right) + R \ln\left(\frac{V_2}{V_1}\right), \frac{V_2}{V_1} = 1$

11. $dS = \frac{\delta Q}{T} = \frac{I^2 R t}{T} = \frac{10^2 \times 25 \times 1}{300}$

12. Entropy change of water (gain)

$$\begin{aligned} dS &= \int_{273}^{373} \frac{\delta Q}{T} = \int_{273}^{373} ms \frac{dT}{T} \\ &= 1 \times 10^3 \int_{273}^{373} \frac{dT}{T} = 10^3 \ln\left(\frac{373}{273}\right) \text{ cal/K} \end{aligned}$$

Entropy change of reservoir (loss)

$$\begin{aligned} dS &= \frac{\delta Q}{T} = ms \frac{dT}{T} \\ &= 1 \times 10^3 \times \frac{(373 - 273)}{373} = 268.1 \text{ cal/K} \end{aligned}$$

Entropy change of the universe

$$= 1311 - 1126 = 185 \text{ JK}^{-1}$$

13. $dS = \frac{\delta Q}{T} = \frac{\frac{1}{2} CV^2}{T} = \frac{\frac{1}{2} \times 10^{-6} \times (100)^2}{273}$

14. $\left(\frac{dT}{dS}\right)_V = \frac{T}{C_V}$ see problem 4

$$\left(\frac{dT}{dS}\right)_P = \frac{T}{C_P} \text{ see problem 5}$$

$$\therefore \frac{(dT/dS)_V}{(dT/dS)_P} = \frac{C_P}{C_V} = \gamma > 1$$

$$\therefore \left(\frac{dT}{dS}\right)_V > \left(\frac{dT}{dS}\right)_P$$

15. Change in entropy of the reservoir at 553 K,

$$dS = \frac{\delta Q}{T} = \frac{100 \times 10^3}{553} = 1808.3$$

Change entropy of the reservoir at 278 K,

$$dS = \frac{\delta Q}{T} = \frac{100 \times 10^3}{278} = 359.71$$

$$\therefore \text{Net change} = 1808.3 - 359.71$$

$$= 1.449 \times 10^3 \text{ JK}^{-1}$$

- 16. See book work
 - 17. See book work
 - 18. See book work
 - 19. See book work
 - 20. See book work
 - 21. See book work
 - 22. See book work
 - 23. See book work
 - 24. See book work
 - 25. See book work
 - 26. See book work
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